

Enhanced Electricity Generation by Using Cheese Whey Wastewater in A Single-chamber Membrane Less Microbial Fuel Cell

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Abstract

Microbial fuel cells (MFCs) are biochemical-catalyzed systems in which electricity is produced by oxidizing biodegradable organic matters in presence of bacteria. Many places suffer from lack of electricity infrastructure or even existence, but in the same area there is wastewater that can be used to generate clean energy. A batch system single chamber and membrane-less microbial fuel cell is designed with wastewater as inoculum and fuel in the same time (before adding cheese whey) at $\text{pH} = 7 \pm 0.4$ and an operating temperature of 30°C . Wastewater samples are collected from the Al-Delmaj marsh site at an initial chemical oxygen demand concentration of 862 mg/l and pH of 7.8 (reduced to 7 ± 0.4 in all experiments by adding HCL acid). Rectangular sheets of graphite and smooth surface carbon fiber of 42 cm^2 surface area used for anode and cathode electrodes. The obtained results indicated that the cell performance for the cell using graphite for anode and cathode electrodes is better than that using the carbon fiber of smooth surface. The obtained open circuit voltage and power per unit surface area (for graphite) were 190 mV and 5.95 mW/m^2 respectively. Cheese whey as substrate was used to enhance the performance of cell to 439 mV OCV and 121.9 mW/m^2 maximum power density.

Keywords : Microbial fuel cell, Biochemical, Cheese whey, Clean energy

الخلاصة

خلايا الوقود الميكروبية هي أنظمة محفزة بطريقة بيو كيميائية والتي فيها الطاقة الكهربائية انتجت من أكسدة المواد العضوية القابلة للتحلل وبوجود البكتيريا. عدة أماكن تفتقر لوجود البنية التحتية للكهرباء أو حتى بوجودها لكن يوجد في نفس المنطقة مياه ملوثة يمكن استعمالها لتوليد طاقة نظيفة. تم تصميم خلية الوقود الميكروبية بنظام الدفعة الواحدة بأسلوب أحادي الحجرة و بدون غشاء فاصل مع استعمال المياه الملوثة كوقود ومصدر للميكروبات بنفس الوقت (قبل إضافة مصل الجبن) في وسط درجة حرارته 30°C والحمضية 7 ± 0.4 . عينات المياه الملوثة أخذت من موقع هور الدلمج عند درجة حمضية 7.8 (خفضت في التجارب إلى 7 ± 0.4 باستعمال حامض كلوريد الهيدروجين) ومقدار كمية الأوكسجين المستهلك كيميائياً الابتدائية 862 mg/l . تم استعمال أقطاب (الموجب والسالب) على شكل شرائح مستطيلة الشكل من الغرافيت و الياف الكربون (ناعمة السطح) بمساحة سطحية 42 سم^2 . بينت النتائج أن أداء الخلية باستعمال الغرافيت (كقطب موجب وسالب) أفضل من استعمال قطب الياف الكربون (ناعمة السطح) كان جهد الدائرة المفتوحة المتحصل (لقطب الغرافيت) 190 mV والقدرة خلال وحدة المساحة 5.95 mW/m^2 . وقد استعمل مصل الجبن كمادة متفاعلة مضافة للمياه الملوثة لتحسين جهد الدائرة المفتوحة للخلية من 190 mV إلى 439 mV و اعظم كثافة طاقة متولدة كانت 121.9 mW/m^2 .

الكلمات المفتاحية: خلية الوقود الميكروبية، البيو كيميائية، مصل اللبن، الطاقة النظيفة.

1.Introduction

Recently, researchers focused on the microbial fuel cells (MFCs) due to their operational and functional advantages over other technologies used for generating current from organic material. In MFCs the direct conversion of substrate to electricity at ambient or even at low operating temperatures enables high conversion efficiency. MFCs are environmentally friendly since they don't require gas treatment (Gupta *et.al.*, 2012). Furthermore, the ability to generate power using bacteria already in the wastewater make MFCs a promising technology for wastewater treatment (Cheng and Logan 2007).

Wastewater needs to be remediated to acceptable contaminants concentrations to be recycled, thus, more economic water treatment processes that are sustainable and their production have a minimum net carbon emission into the ecosystem can be achieved by applying the anaerobic based treatment technique in which the bioremediation of wastewater produces energy rich by products in the form of reduced protons or hydrogen and which is usually a substrate for methane production. However, the reducing potential generated in anaerobic digestion can be used to directly generate electricity in MFC reactors (Mahlangu, 2015).

Anaerobic wastewater treatment employs the catalytic action of anaerobic bacteria to break down complex reduced compounds found in various industrial effluents into monomers which are less or non toxic and easier to degrade with traditional anaerobic water treatment processes. This degradation of reduced compounds by bacteria is accompanied by a release of energy. This informs the current efforts to attempt to couple wastewater bioremediation and biofuel production (Mahlangu, 2015).

Several types of substrate have been studied in MFCs for bioelectricity generation. With growing concerns for exploring other energy sources, waste management, global climate change, and no edible feedstocks, searches for novel technical solutions are in progress. Fuel cells are the alternative energy extractor technology that is studied for a full-scale implementation (Nasirahmadi and Safekordi, 2012).

The produced bioelectricity varies from different substrates according to the source of substrates. Cheese manufacturing industry generates large amounts of high strength wastewater characterized by a high biological oxygen demand (BOD) and COD concentrations (Nasirahmadi and Safekordi, 2012).

Cheese whey is the liquid fraction which remains after the precipitation and removal of milk casein, during the cheese-making process, with chemical oxygen demand (COD) reach to 6.7 g/L. It contains a significant amount of carbohydrates of 4–5%, mainly lactose, proteins no more than 1%, fats at about 0.4 – 0.5%, lactic acid less than 1% and salts that may range from 1% up to 3%. Nowadays, the cheese manufacturing industry generates large quantities of this high strength wastewater, the disposal of which constitutes serious environmental problems (Tremouli *et.al.*, 2013).

2. Materials And Methods

The electrochemical cell constructed in this work is a single chamber membrane; less fabricated from Plastic in a semispherical shape as it is shown schematically in Figures 2.1.

The cell reactor volume (1400 ml) incorporates a 700 ml of electrolyte and the anode and cathode electrodes of a similar shape, size and material. 2 cm spacing is maintained between the two electrodes with no membrane. The two electrodes are connected to an insulated copper wire by rubber insulator to avoid water leakage and then fitted to the sealed reactor to achieve an anaerobic system. The reactor is assembled with recirculation tubes, air pump, voltmeter and variable resistances.

The electrodes are made from two rectangular shapes of graphite plates (42 cm²) and carbon fiber sheet (smooth surface area) with (42 cm²) surface area.

Electrolyte of the cell stabilized at a temperature of 30 °C, which is the optimum temperature for the bacteria to be active (Yu *et.al.*, 2012), by using water bath. Air is supplied to the cathode side by an external air pump. A mechanical recirculation pump was used to produce well mixed conditions within the MEC reactor.

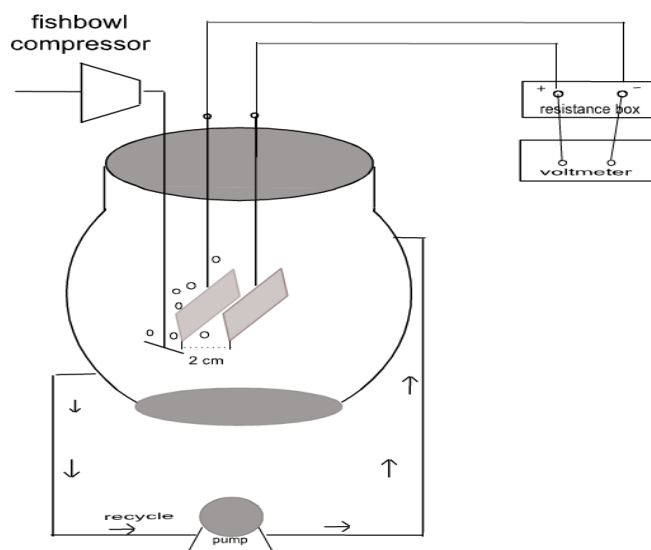


Fig. 2.1: Schematic Shape for Microbial Fuel Cell

2.1 Wastewater and Organic Substrate

Wastewater samples are collected from the Al-Delmaj marsh site with 862 mg/l initial COD concentration at pH of 7.8 reduced to 7 ± 0.4 in all experiments by using HCl acid. Wastewater is used as an inoculum for the reactor and as well as a fuel at the same time (before adding cheese whey). Cheese whey is added to the wastewater as a substrate to enhance MFC energy generation .

2.2 Microorganisms Test

To identify the type of bacteria and other microorganisms living in the wastewater samples, an examination is conducted at the Biological Department Laboratories/ College of Science at the University of Babylon. Staphylococcus aureus, E.coli, pseudomonas and yeasts (candida albicans) are identified throughout the test .

2.3 The Experiment Procedure

The MFC is designed and assembled as it is shown in Figure 2.1, incorporating two rectangular plates of graphite each has a surface area of 42 cm^2 used for anode and cathode electrodes . The wastewater is added to the cell chamber which is tightly sealed and then the OCV values are taken at 2 hrs interval until the steady state voltage is reached . Polarization data are obtained using an adjustable external resistance after OCV steady state to determine variation of voltage vs current density.

The same procedure is followed using two rectangular sheets of carbon fiber each has a smooth surface area of 42 cm^2 for anode and cathode electrodes to find out which electrode material gives a better performance to accomplish the following experiments with it.

Cheese whey as a substrate at a concentration of 100 ml is added to the wastewater and then the OCV values and the polarization data are taken in the same procedure aforementioned.

Current and power are calculated based on following equations (Rahimnejad *et. al.*, 2011) :

$$I = E/R_{\text{ext}} \quad \dots\dots\dots 2.1$$

$$P = I \times E \quad \dots\dots\dots 2.2$$

Where I represents the produced current, E is the measured cell voltage at 4 minutes interval (which mean 4 min. for each resistance), R_{ext} denotes the external resistance ranged $100\text{ M}\Omega$ - $50\text{ }\Omega$ and P is the generated power. Then the current density and power per unit surface area can be obtained by dividing current and power on the anode surface area.

3. Results and Discussion

Polarization curves for the fabricated MFC are plotted at several external resistances to determine the maximum power generated. To enhance the cell performance, cheese whey as a substrate is added to the electrolyte.

3.1 Cell Performance without any Additives

Two couples of similar size, shape and materials for anode and cathode electrodes are examined to identify which electrode material gives the better performance. Graphite and carbon fibers of smooth surfaces are the selected materials for electrodes.

Figure 3.1 shows the cell voltage vs. time curve of a microbial fuel cell with graphite and smooth carbon fiber electrodes at an operating temperature of $T=30\text{ }^{\circ}\text{C}$ and $\text{pH}=7\pm0.4$ for the wastewater without any additives. Clearly, the graphite/graphite couple shows a better performance than the carbon fiber/carbon fiber couple does due to the smooth surface of the carbon fiber which affects the formation of the biofilm. Initially, the recorded open-circuit voltage is 45 mV then the cell voltage starts to stabilize after 34 hours of operation at a value of at 190 mV due to the higher rate required for the microorganism to form the biofilm on the surface of the electrode. Then, the cell voltage decreases as a result of the competition between the microorganisms to obtain their food from the organic matter and nutrients in the wastewater. This behavior agrees with the published results recorded by (Hisham *et. al.*, 2013; Mohan *et. al.*, 2008).

Based on these results, the remaining experiments are performed using graphite materials for both anode and cathode electrodes.

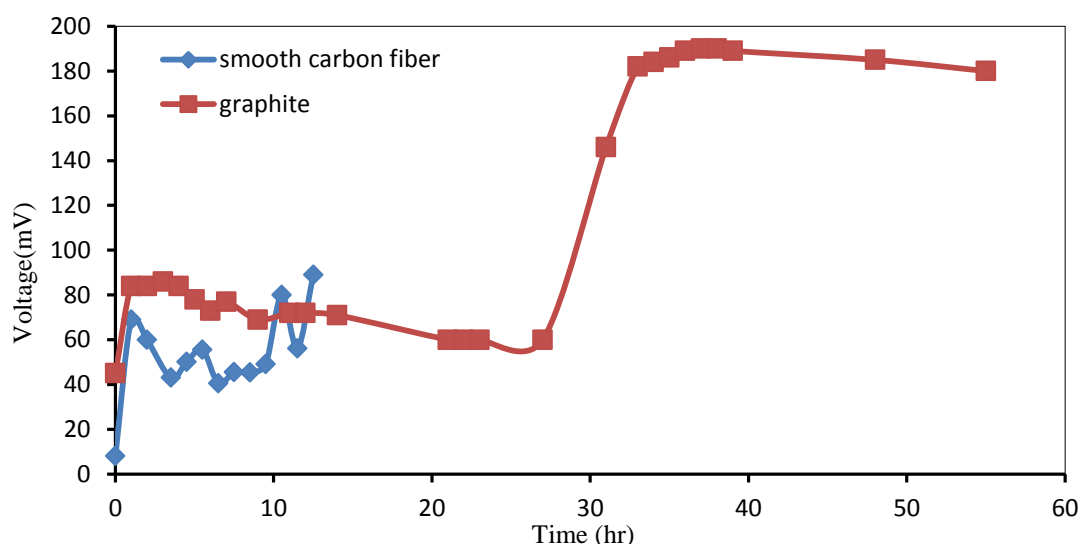


Figure 3.1: Cell Voltage vs. Time for The Microbial Fuel Cell Using Graphite And Smooth Carbon Fiber Electrodes at an Operating Temperature of $T=30\text{ }^{\circ}\text{C}$, $\text{pH}=7\pm0.4$ and Wastewater Without any Additive.

Figures 3.2 and 3.3 show the polarization curves and power density recorded for graphite/graphite electrodes with wastewater as inoculation and a fuel at the same time without any additives at an operating temperature of $T=30^{\circ}\text{C}$ and $\text{pH}=7\pm0.4$. The maximum produced power is 5.95 mW/m^2 .

An 'overshoot' phenomenon is observed in figure (3.3) while the perfect power curve should show the power rising to a peak point before dropping as the current increases in a semi-circle fashion .

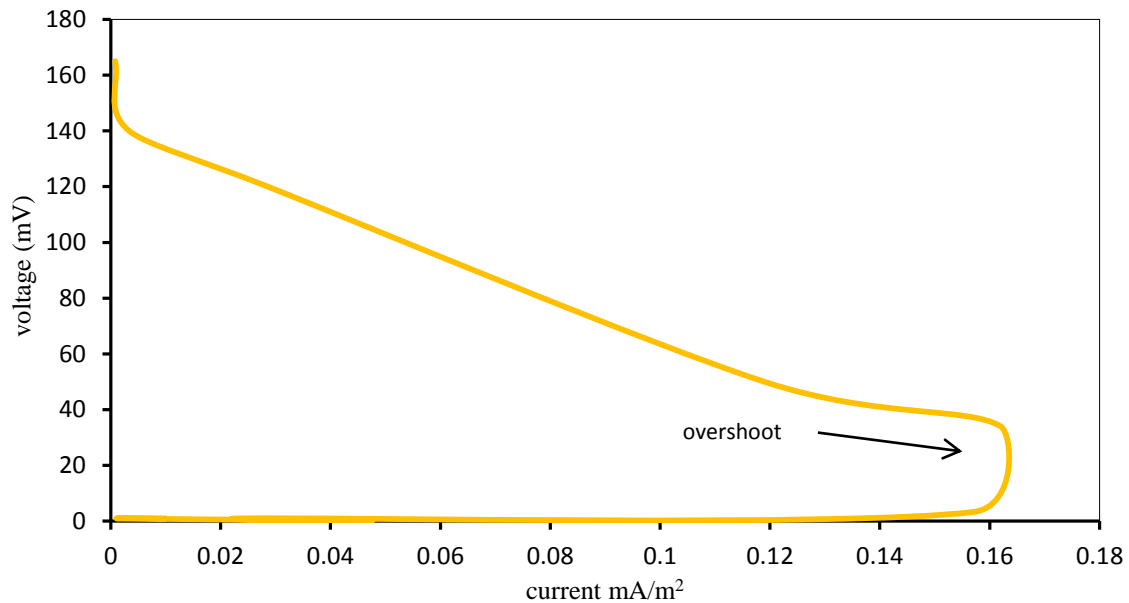


Figure 3.2: Voltage vs. Current Density Curve for the Microbial Fuel Cell Using Graphite Electrodes at an Operating Temperature of $T=30^{\circ}\text{C}$, $\text{pH}=7\pm0.4$ and Wastewater Without any Additive.

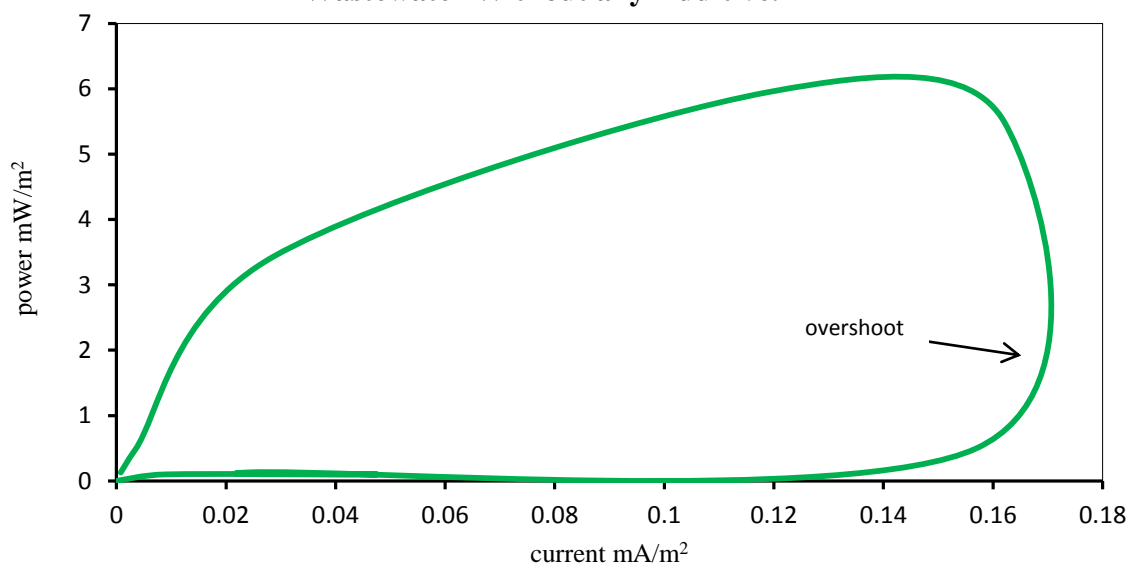


Figure 3.3: Power Density vs. Current Density Curve for the Microbial Fuel Cell Using Graphite Electrodes at an Operating Temperature of $T=30^{\circ}\text{C}$, $\text{pH}=7\pm0.4$ and Wastewater Without any Additive.

An explanation for the phenomenon was showed in the published work of Min *et.al.*, (Min *et.al.*, 2008) who hypothesized that the overshoot might be the result of mass transport limitation in the anode .

The hypothesis formulated in the present study, is that the overshoot phenomenon is a result of both electrical and ionic depletion effected primarily by the lower ('heavier') values of the resistance range . In this study it has been repeatedly noticed that the retracting ('bending inwards') part of the power curve occurs at the point where the scale of the load step-changes , decreases, i.e. when the range switches from thousands to hundreds which agrees with the published results by Ieropoulos *et.al.*, (Ieropoulos *et.al.*,2010). At these lower resistive values , the demand for electrons due to the more conductive external path exceeds the microbial rate that they can be supplied at , and as a consequence , the anolyte becomes depleted of electrons and ions .

3.2 Cell Performance Using Cheese Whey as a Substrate

Increasing the concentration of the cheese whey (CW) substrate was reported by Tremouli *et.al.*, (Tremouli *et.al.*, 2013) to affect the duration of the operation cycle with practically no noticeable change in potential values.

To insure no change in pH of the electrolyte, a 100 ml of CW is added as a substrate to investigate its effect on the performance of the fabricated MFC.

Comparing Figure (3.4) with Figure (3.1), a remarkable change is noticed in both the trend and the voltage values. The initial voltage increased to a value of 420 mV and the open circuit voltage starts to stabilize after 26 hours to reach a value of 439 mV.

Within the first two hours of operation, a sudden drop in cell voltage is marked due to the presence of unusable electrons (often because of the lack of a final electron receptor, such as oxygen) saved in the electrons transport chain of the microorganism cells and consequently, the competition occurs between the microorganisms to obtain their food from the organic matter and nutrients in the wastewater . Furthermore, the exoelectrogens in the wastewater are capable of forming a biofilm for electron transfer to the surface of the electrode at a more efficient rate and voltage drops due to that competition as explained by Hisham *et.al.*, (Hisham *et.al.*, 2013).

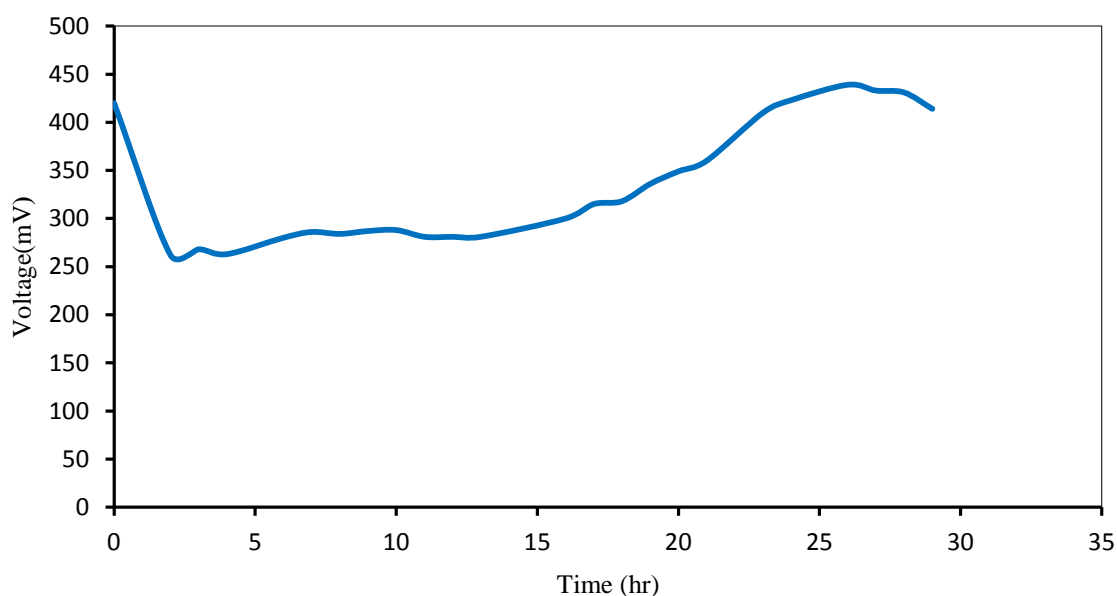


Figure 3.4: Cell Voltage vs. Time of the Microbial Fuel Cell Using Wastewater with 100 ml Chees Whey with Graphite Electrodes at an Operating Temperature of $T=30^{\circ}\text{C}$ and $\text{pH}=7\pm0.4$.

The cell voltage vs. current density and the power density vs. current density curves for the MFC using cheese whey as a substrate are presented in Figures 3.5 and (3.6). Experimental are carried out by varying the external loads . Readings are taken after the addition of fresh substrates and when the MFC reached a stable operation (plateaus in Figure (3.4)) . The maximum power density (normalized to the geometric area of the anodic electrode) is found to be 121.9 mW/m^2 , The ‘overshoot’ phenomenon observed in Figures (3.5) and (3.6) is due to the same reasons discussed in section (3.1) above .

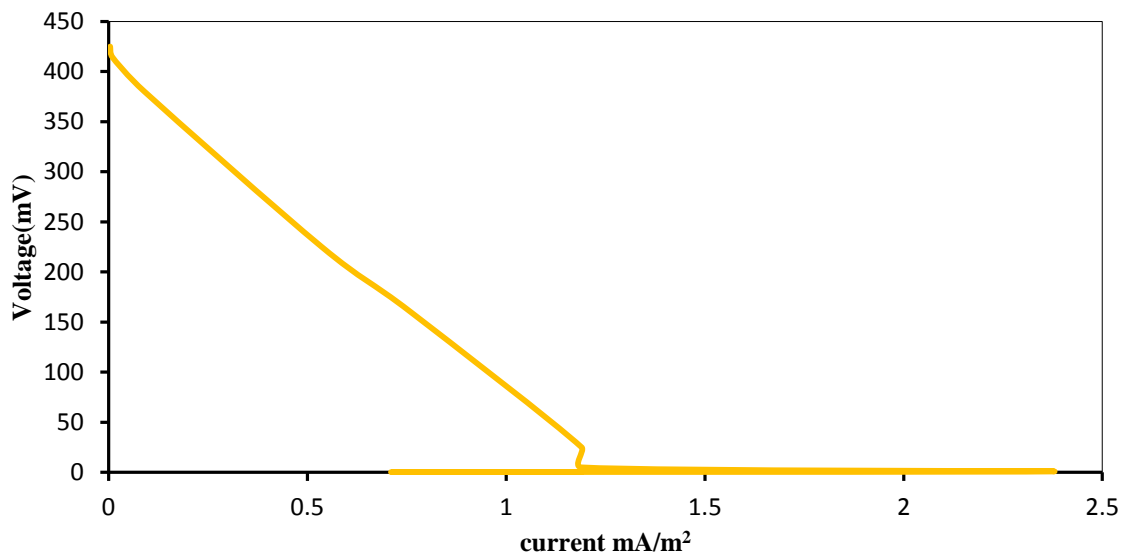


Figure 3.5: Voltage vs. Current Density for the Microbial Fuel Cell by Adding a 100 ml Cheese Whey to the Wastewater with Graphite Electrodes at an Operating Temperature of $T=30^{\circ}\text{C}$ and $\text{pH}=7\pm0.4$.

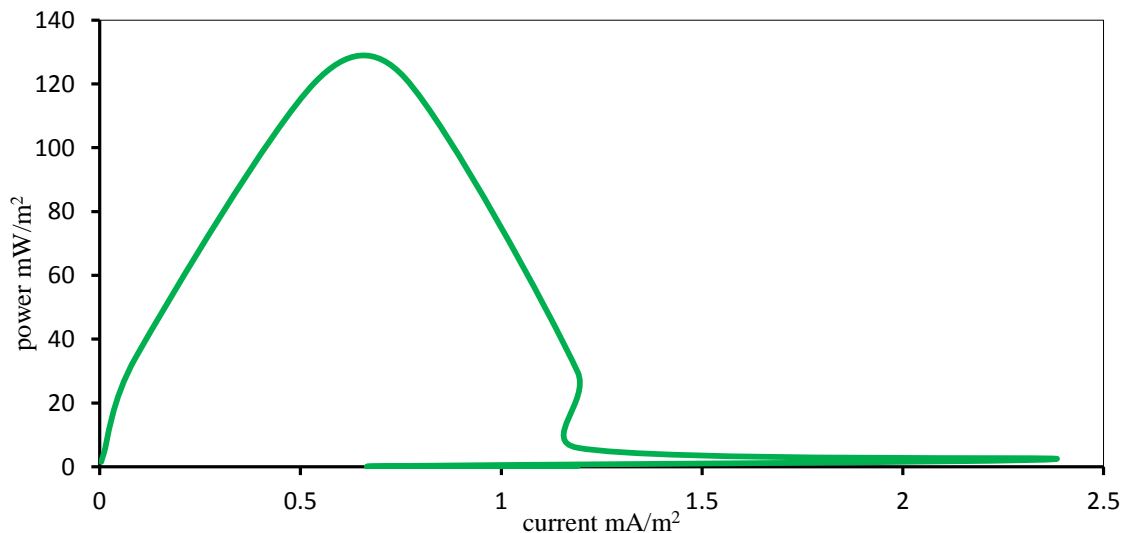


Figure 3.6: Power Density vs. Current Density for the Microbial Fuel Cell by Adding a 100 ml Cheese Whey to the Wastewater with Graphite Electrodes at an Operating Temperature of $T=30^{\circ}\text{C}$ and $\text{pH}=7\pm0.4$.

5.1 Conclusions

Throughout the results presented and discussed in the previous section, the following remarks can be concluded:

- 1- The MFC produces much power by using graphite to fabricate the anode and cathode electrodes.
- 2- Cheese whey as a substrate has a great effect on the MFC voltage and small effect on the cell power production.

Acknowledgements

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